ON THE THERMAL DEVELOPMENT OF THE SPARK SPECTRUM OF CARBON.

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During the course of some experiments which Professor Basquin was making on the production of arc and spark spectra from the same electrodes, it was observed by one of us, standing at the eyepiece of his spectroscope, that the lines of the spark spectrum made their appearance gradually, and not suddenly, beginning at the instant at which the direct current feeding the arc was cut off and the high-voltage current producing the spark was switched on.

It was evident at once that the appearance of these lines in deliberate succession was due, primarily at least, to the gradual cooling of the electrodes and of the region between them. But we were uncertain whether, after all, the effect was not merely a physiological one, the lines first observed being the stronger lines, and those observed later being the weaker lines. We accordingly set about making a series of photographs which should show the spark spectrum at each successive instant beginning at the time at which the arc current is interrupted.

At first our attempt was to employ metallic spark-electrodes for the spectrum and to use the carbon arc to heat the spark gap. And in order to retard the development of the spark as much as possible, the carbon electrodes were enclosed between two saucer-shaped clay scorifiers as shown in Figure 1. The terminals of the spark circuit were introduced into this cell at right angles to those of the arc. Various other forms of cells, hollowed limes from the stereopticon, clay pipes, fire brick,

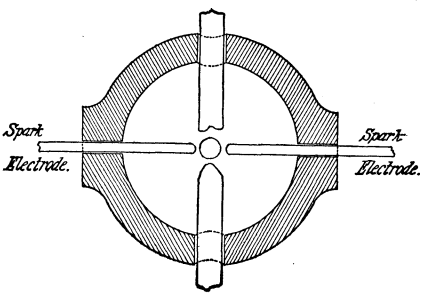

Figure 1.

etc., were tried. But in each case, as soon as the region inside got hot enough to affect the character of the spark and render it quiet, we found (as, indeed, ought to have been anticipated) that the walls of the vessel became conducting.

We tried next to get a gradual variation of temperature by moving the spark gap slowly from the centre to the edge of an ordinary carbon arc, knowing that, at the centre of the arc, the spark was quiet and non-luminous, while just outside the arc it became noisy and brilliant. But in carrying the spark electrodes from one of these positions to the other, we encountered a peculiar discontinuity, i. e. a position at which the spark *instantly* changed character.

When the spark was passed through the "horsetail" above the horizontal arc at a distance of from $\frac{1}{2}$ to 2 centimeters from the arc, the quiet discharge mentioned above was still obtained and a spectrum of feeble intensity could be observed. When, however, the terminals were removed slightly farther above the arc, a point was reached at which the discharge instantly assumed the ragged character of the ordinary cold spark; and when the spark was then moved back toward the arc it did not resume its quiet character, but blew the "horsetail" away, and in most cases put out the arc. It did not seem possible to obtain any intermediate stages. The instability was very marked. The spark was liable at any time to break down into the ragged character, and when it had once done so it retained that character until the circuit was broken.

Apparatus and Method.

Accordingly we had recourse to soft-cored carbons worked in air, *using the same electrodes for both arc and spark;* in other words, we used the hot region between the poles of an ordinary carbon arc as the heated medium in which to study the slowly developing spark.

The next step consisted in isolating the particular phase of the development which we wished to examine.

This was accomplished by means of a device (designed with the generous aid of Professor Basquin) which performs automatically the following cycle of operations: —

1. Closes the arc circuit and lights the arc, thus heating the carbon electrodes and the region between them to a very high temperature.

2. After an interval of a few seconds, sufficient for the carbons to become thoroughly heated, interrupts the arc circuit.

3. After an interval which is less than one-tenth of a second, closes the spark circuit.

4. After a variable (but definite and measurable) interval of time, opens a shutter in front of the slit of the spectroscope and exposes the plate during any desired length of time, generally between $\frac{1}{2}$ second and 1 second.

5. Interrupts the spark circuit.

1. Again closes the arc circuit; and so on, as before.

The arc was operated with 15 amperes showing 40 volts between the electrodes; while the spark was produced by a large induction coil of the type devised by Rowland in 1887 and described in Kayser's Handbuch der Spectroscopie, p. 183. This induction coil, or step-up transformer, was operated on a 104-volt alternating circuit, of frequency 120, with a primary current of 20 amperes. In parallel with the spark gap was placed a capacity of $\frac{1}{50}$ microfarad. The arrangement of the circuit is shown in Figure 2 where s_1 and s_2 are each double pole mercury switches so fixed that *one can be closed only after the other is opened.* s_1 is kept closed by a spring until an electromagnet begins to close s_2 by rocking a light beam of which its armature is a part. The question of changing from arc to spark circuit is then merely a question of closing the battery circuit which actuates this electromagnet. This battery circuit is closed and opened by a continuously rotating switch (shown at the left in Figure 3) which is driven at the uniform rate of 10 R. P. M. by a small electric motor. This rate of rotation is maintained constant by means of a pair of cone pulleys and a heavy flywheel.

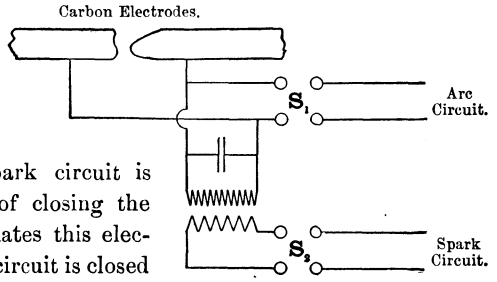

FIGURE 2.

This same rotating switch, or commutator, by means of the sliding contact marked "2" in Figures 3 and 5, opens the shutter in front of the slit of the spectroscope at any phase of the spark desired and holds the shutter open for a small but definite period of time varying usually from $\frac{1}{2}$ second to 1 second. On this same rotating commutator shaft is a stud (D, Figure 3) which, immediately after the arc circuit is closed, pushes a carbon rod into the arc gap for an instant and thus "lights" the arc.

By clamping the sector P (Figure 5) to the rotating commutator in successive angular positions about its axis, one is enabled to open the slit

for the successive phases of the spark which he may wish to photograph; not only so, but he can repeat any phase as many times as he likes, and thus obtain a strong composite in cases where a single exposure would produce no visible effect.

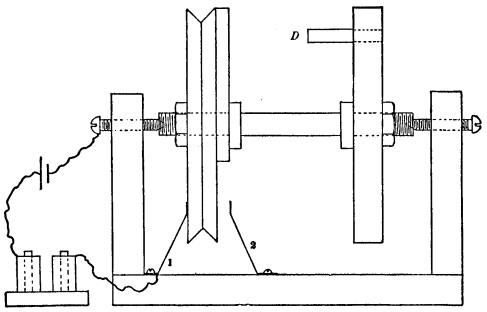

FIGURE 3.

In this manner we have photographed the spark spectrum of carbon, with a ten-foot concave grating, in nine different phases,* which may be roughly described as follows: —

1. Exposure begins $\frac{1}{8}$ second after breaking arc and lasts $\frac{1}{2}$ second. Here the carbon poles are still white hot and the spark is practically silent when compared with the noise which the cold spark makes. In this stage the luminosity is so exceedingly feeble that, with a slit of the same width as in the rest of the series, six to ten hours (i. e. about 5000 exposures) are required to get a fair negative.

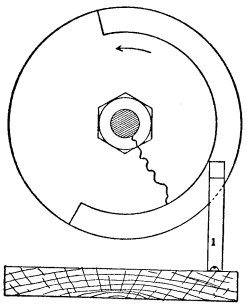

FIGURE 4.

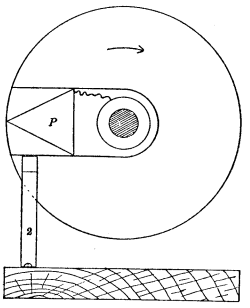

FIGURE 5.

2. Exposure begins $\frac{1}{4}$ second after breaking of arc and lasts for 1 second. The middle of the exposure, therefore, occurs $\frac{3}{4}$ second after the beginning of the spark. Here, again, the image of the spark on the slit of the spectroscope is quite invisible during the entire exposure.

* The purpose of this experiment, it will be observed, is therefore fundamentally different from that in which Sir Norman Lockyer examined the spark spectra of salts volatilized in flames and which he described in Proc. Roy. Soc., **30**, pp. 22-31 (1879).

3. Exposure begins $\frac{1}{2}$ second after breaking of arc, and lasts for 1 second; middle of exposure one second after beginning of spark. Here the image of the spark is barely visible just before the slit is covered. The spark is distinctly louder than in the preceding phases.

4. Middle of exposure $1\frac{1}{4}$ seconds after beginning of spark.

5. Middle of exposure $1\frac{3}{4}$ seconds after beginning of spark.

6. Middle of exposure $2\frac{5}{8}$ seconds after starting spark.

7. Middle of exposure $5\frac{1}{4}$ seconds after starting spark. Here the electrodes begin to show merely red, instead of white, hot.

8. Middle of exposure $7\frac{7}{8}$ seconds after beginning: spark distinctly noisy.

9. The last photograph in the series was taken at twelve seconds after the beginning of the spark, the duration of the exposure being, as in the preceding cases, one second. Even at this late stage a distinct *crescendo* is still noticeable in the noise of the spark.

The enormous increase of brilliancy from the hot spark to the cold may be judged from the fact that in order to make the cyanogen band at λ 3883 of uniform intensity the exposure time for the first of the series was eight hours and for the last of the series twenty minutes.

Results.

As in the case of the Swan spectrum and the carbon arc, so also in the case of the carbon spark, the flutings are, of course, the dominant features of the entire spectrum. The first question, therefore, which naturally arises, in the development of the spark, is concerning the order and the relative intensity in which these cyanogen bands make their appearance. A second question might be asked concerning the stage at which the air lines make their appearance. A third query is when and how do the numerous metallic impurities present themselves? Our photographs permit at least partial answers to these three questions for the region lying between λ 4500 and λ 3000. The phenomenon is one which cannot be accurately observed by the eye, and the exposure times are so long as to render photographing in the visible region well-nigh impracticable.

I. Carbon Flutings and Lines.

The cyanogen bands at $\lambda\lambda$ 4216, 3883, and 3590 all make their appearance on the first photograph of the series. Their relative intensity is practically the same as in the case of the spark between cold electrodes, which, for the sake of brevity, we shall hereafter call the

"cold spark." In view of this fact we have employed these three bands as standards of intensity; and have called any two spectra of "equal intensity" when these three bands were of equal intensities on the respective negatives. Each member of the series was, in this way, made of practically the same intensity.

As to the carbon lines, very few appear in this region. The line at λ 4556.3 does not appear in the hot spark, i. e. in the earliest phase of the series described above. The broad hazy line at λ 4267.5, which Eder and Valenta* call the "chief carbon line," disappears completely on introducing inductance into the circuit of the cold spark. And it does not appear at all in the hot spark. These two facts raise the question as to whether this line is due to carbon. The line at λ 3361 persists in the hot spark; but it also appears in the aluminium spark and, greatly enhanced, in the copper spark when there is no capacity in the circuit. As to the remaining lines which Eder and Valenta describe in this region λλ 3920.8, 3877.0, and 3848.0, they are weak, and we have not been able to identify them to our satisfaction.

II. Air Lines and Flutings.

Not one of the ordinary air lines appears on any photograph whose phase is earlier than $\frac{3}{4}$ second. On the plate whose phase is $\frac{3}{4}$ second appear only the very heaviest of the air lines, viz., λλ 4630: 4447: 3995: 3433: 3330. Indeed the elimination of air lines is so complete in these earlier phases that non-appearance in the hot spark might be used as one criterion for air lines, analogous to the inductance test discovered by Schuster and Hemsalech.

As to nitrogen *flutings* which appear in spark spectra, when the electrodes are close together or when inductance is placed in series with the condenser, the case is very different — quite reversed, indeed — from that of ordinary air lines. The nitrogen flutings with heads at λλ 3371.1 and 3158.7 respectively come out very strong in the earliest phase; at $\frac{3}{4}$ second they begin to weaken; after 3 seconds, only a trace of them is left.

The nitrogen flutings of wave-length longer than 3371 do not appear in the spark under the conditions in which we are working, namely, a 3-millimeter spark gap in series with a condenser of $\frac{1}{50}$ microfarad capacity; no inductance.

We have not found any description of these nitrogen bands *as they*

* Eder and Valenta, Denksch. K. Akad. Wien, **60**, 249 (1893).

appear in the spark spectra of elements in air at barometric pressure. At first we took the band at λ 3371.1 to be a hitherto undescribed carbon band; and it was only through an excellent suggestion from Professor Hale that we discovered our mistake. He advised us to try the spark *without capacity.* On trying this experiment, we found the band at λ 3371.1 strongly present in the spectra of aluminium, zinc, and other metals in air; but when the spark was worked in atmospheres of oxygen or coal gas, these flutings all disappeared save the merest trace of the strongest two.

The cold carbon spark (unlike that of metals) without capacity shows these bands only with extreme faintness; and the condensed carbon spark does not show them at all; but *carbon when white hot shows them strongly,* as indicated above.

In this connection, the question may be raised whether the band described by Professor Hutchins * does not belong to this nitrogen group. For we have found in the spark spectrum of aluminium a band, with its edge at λ 3914.41, which shows a weak line alternating with a strong one exactly as in Hutchins's photograph. But on examining this spark in a current of oxygen, not the slightest trace of the band was found. Since it is found in metals, but not in the carbon spark, and since it disappears when nitrogen disappears, it seems to us more probably due to nitrogen † than to carbon.

What is apparently the same band may be seen very distinctly on McClean's map of the spark spectrum of copper; and again a similar fluting has been found by Deslandres at the negative electrode of a spectrum tube filled with nitrogen. For Deslandres' drawing see *Comptes rendus,* 9 Aug., 1886. This is probably also the same band

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* Hutchins, Astrophysical Journal, **15**, 310 (1902).

† Mr. F. J. Truby has measured the first 14 lines of this fluting, which form a group lying between the edge and the heavy impurity line at λ 3905.74. His values are as follows:

3914.41, head	3909.95, weak
3913.89	3909.30, strong
3913.35	3908.52, weak
3912.62, strong	3907.80, strong
3912.17, weak	3906.88, weak
3911.70, strong	3906.16, strong
3911.17, weak	3905.74, impurity
3910.61, strong	

There are possibly two other weak lines near the head which Mr. Truby's definition does not permit him to measure.

which is marked *very strong* at λ 3914.4 in Hemsalech's* table of nitrogen bands. The fact that Hutchins is able to intensify the band he describes by making and breaking the arc circuit would seem to indicate that it appears in the arc spectrum primarily in consequence of high electromotive force.

III. Metallic Impurities.

The only electrodes which we have employed are the unplated, cored carbons sold by A. T. Thompson, 25 Bromfield St., Boston, for use in projection lanterns. Their size is $7\frac{1}{2} \times \frac{1}{2}$ inches and they are marked "imported." The metallic impurities which present themselves are practically only aluminium, calcium, copper, iron, and potassium. Possibly others might be detected by very long exposure or by study of portions of the spectrum other than that to which we have limited ourselves, namely, λ 4500–λ 3200. The strongest lines in this region of the hot spark spectrum are two at λ 4047.338 and λ 4044.294 belonging to the principal series of potassium. They are faintly represented in the carbon arc; but *no trace of them can be found in the ordinary, or "cold," carbon spark.* Is it not rather surprising to find on a spark spectrum plate that the strongest lines are due not only to an impurity, but to an impurity which is introduced apparently by the condition of high temperature in the medium? For, so far as the energy delivered by the spark itself is concerned, this would seem to be enormously greater in the loud and brilliant cold spark than in the quiet and invisible hot spark. We use the expression "high temperature" in this connection only with great hesitation, and then only with reference to the medium after the heating current has been cut off. *But this potassium pair persists very distinctly for five seconds after the heating (arc) current has been interrupted.* Accordingly we find it difficult to imagine any electrical effect, other than heat, which would persist for this length of time, especially, as the electrodes were placed always horizontally so that strong convection currents were sweeping out anything in the nature of electrolytic products.

It seems not improbable that these effects of the hot spark are brought about through an increased conductivity — and hence a lowered electromotive force — between the poles of the spark gap. So that, in the series described above, the earlier phases partake of the character of the

* Hemsalech, Recherches expérimentales sur les spectres, etc., p. 126 (Paris, 1901).

arc, while the later phases represent the spark. *If this be true, the nine members of this series constitute nine different steps between the arc and the spark spectra.*

A similar diminution of E. M. F. between the hot poles is indicated by the work of Schenck, * who finds that, with hot poles, the "Mg. spark line at λ 4481 shrinks down close to the electrodes, while the arc triplet at λ 5170 does not." And this view is rendered all the more probable by a fact noted by Basquin, † viz. that an auxiliary cold spark gap, in series with the hot spark gap, suffices to render the spark lines immediately visible.

The general effect of the hot spark upon metallic impurities may perhaps be most clearly described in the following three statements:

1. Some *new* impurities are introduced, e. g. Potassium λλ 4047.34, 4044.29, 3447.49, 3446.49. This is analogous to the introduction of the nitrogen fluting at λ 3371 above mentioned.

2. Among lines *due to a single element* some may be diminished while others are enhanced in intensity. Thus the calcium pair at λλ 3968.6 and 3933.8, and also the calcium pair at λλ 3179.4 and 3159.0, are immensely diminished, while the calcium line at λ 4226.9 is so greatly enhanced by the hot spark that, after the potassium pair, it becomes the strongest in the entire region studied. It is perhaps worth noting that all of the lines belonging to any one of Kayser and Runge's series are similarly affected. It would be interesting to know just how this behavior of potassium and calcium is explained in terms of the dissociation hypothesis.

3. The lines of some elements are affected either not at all, or very slightly, by the hot spark. This class is illustrated by the omnipresent copper pair at λλ 3274 and 3247; also by the aluminium pair between Fraunhofer's H and K; and by the great majority of the iron lines.

In general, it may be noted that there is nothing in the nature of a sudden change anywhere in the series. Indeed the growth of the air lines and the diminution of certain impurity lines is so gradual and definite that one might use their relative intensities to determine the phase at which any particular photograph was taken. The triplet formed by the potassium pair at λλ 4047 and 4044, together with the strong iron line between them, serve to illustrate this principle and also to point out an exception to the rule that the iron lines are generally unaffected by the hot spark. For curiously enough *this iron line increases* in intensity as the spark-gap (the medium) cools down, while, as noted above, *the*

* Schenk, Astroph. Jour., **14**, 131 (1901). † Basquin, Ibid., **14**, 15 (1901).

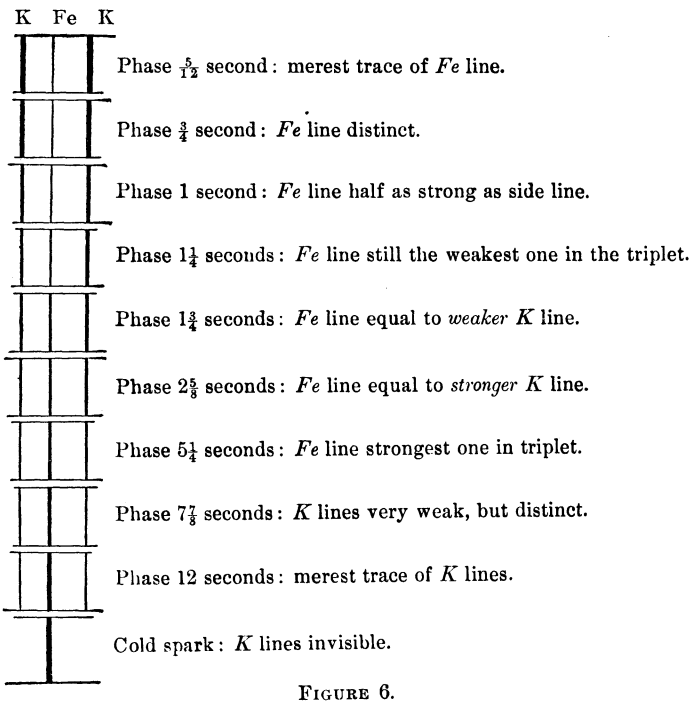

FIGURE 6.

potassium pair diminishes with the temperature. In this comparison the three cyanogen bands are taken as the standard of intensity, and have essentially the same density on each plate. The triplet thus assumes the successive appearances shown in the accompanying figure. If we had measured the temperature of the region between the carbon poles at each of these nine phases, we could have identified with certainty each of these temperatures from the appearance (relative intensity) of the triplet. It is not to be forgotten that the temperature here referred to is *not* the much-talked-of and little-understood "temperature of the spark;" nor is it any temperature peculiar to certain "streaks" as perhaps is the case in the Geissler tube discharge. The temperature here referred to is that of the medium at the instant in which the shutter of the spectrograph is opened. The appearance of this triplet is then a criterion for a temperature which may be measured directly with a thermo-electric couple of sufficiently fine wire; it is a function of the phase, and not of the duration, of the exposure.

NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS,
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